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C₆₀ thin film transistors

R. C. Haddon, A. S. Perel, R. C. Morris, T. T. M. Palstra, A. F. Hebard,
and R. M. Fleming

AT&T Bell Laboratories, Murray Hill, New Jersey 07974-0636

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N-channel field effect transistors with excellent device characteristics have been fabricated by utilizing C₆₀ as the active element. Measurements on C₆₀ thin films in ultrahigh vacuum show on-off ratios as high as 10⁶ and field effect mobilities up to 0.08 cm²/V s. © 1995 American Institute of Physics.

Organic semiconductors are being tested as the active electronic elements of thin film field effect transistors (TFTs), and light emitting diodes.¹⁻⁴ Hole mobilities of 0.07 and 0.22 cm²/V s have been reported for thin film transistors fabricated from α , ω -di(hexyl)sexithiophene,¹ and polythienylenevinylene,² respectively. Fullerene films have also been utilized as the active element in thin film field effect transistors, although the mobilities were found to be rather low (10⁻⁴ cm²/V s).⁵ In the present work we report studies of C₆₀ thin films that have been grown and studied in ultrahigh vacuum, which show that the fullerenes exhibit excellent device characteristics in this environment.

We followed the general scheme adopted to study metal doped C₆₀ films in UHV.⁶ The UHV chamber used in this work is equipped with a C₆₀ source so that the C₆₀ films were grown *in situ* and were not exposed to oxygen prior to their evaluation in field effect devices. Films produced in this way consist of random polycrystalline grains of dimension ~60 Å.⁷ The UHV chamber also contains a quartz crystal microbalance so that we could directly monitor the amount of C₆₀ that was deposited. The system was baked prior to deposition and the base pressure was below 10⁻⁸ Torr.

The field effect measurements were carried out using devices that were similar to those described previously.⁵ The substrates were fabricated from heavily *n*-type doped silicon wafers which were oxidized to leave a 3000 Å thick layer of silicon dioxide on one surface. On top of this surface, chromium (250 Å) and gold (250 Å) pads were deposited using lithographic techniques to give the source (*S*) and drain (*D*) electrodes. The substrates were wired to an UHV feedthrough similar to those used for conductivity studies⁶ and the C₆₀ films were deposited through a shadow mask.

The *n*-channel transistor characteristics of an 800 Å thick film of C₆₀ are shown in Figs. 1 and 2. For a given gate voltage (*V_G*), an ideal field effect transistor (FET) is expected to show a drain current (*I_D*), that increases linearly with drain-source voltage (*V_{DS}*) before gradually leveling off to approach the saturation current (*I_D^{sat}*). The saturation regions are clearly visible in Fig. 1, but the linear region is displaced to high values of the voltage in these devices. This corresponds to the threshold voltage (*V_T*), in conventional MOSFETs, as expressed in Eq. (1);

$$I_D^{\text{sat}} = \mu \left(\frac{CW}{2L} \right) (V_G - V_T)^2, \quad (1)$$

where μ is the channel mobility, *C* is the capacitance of the

gate oxide layer, *W* is the channel width, and *L* is the channel length. For the devices reported in this work these parameters had values of *C*=1.2×10⁻⁸ F/cm², *W*=0.4 cm, and *L*=10 μm. Figure 2 shows a plot of (*I_D^{sat}*)^{1/2} versus *V_G* and the resulting values of the field effect mobility of the electrons (μ_e) and the threshold voltage (*V_T*). This analysis delineates the high threshold voltage necessary for the operation of these devices. The injection of electrons into organic materials via high work function metals is known to be a difficult process from studies of organic light emitting diodes which require electron injection into the conduction band for their operation.^{4,8,9}

Measured at 1 V, the conductivity of the C₆₀ film in Figs. 1 and 2, has a value of 6×10⁻⁸ S/cm. The measured film conductivities vary by about two orders of magnitude and are not ohmic above about 1 V. Figure 3(a) shows the current passed between the source-drain contacts of a TFT during the deposition of a C₆₀ film at a constant bias of *V_{DS}*=10 V. Whereas Fig. 3(b) shows the apparent conductivity (σ_{ap}), calculated from Fig. 3(a) by combining the measured film thickness with the other geometric parameters

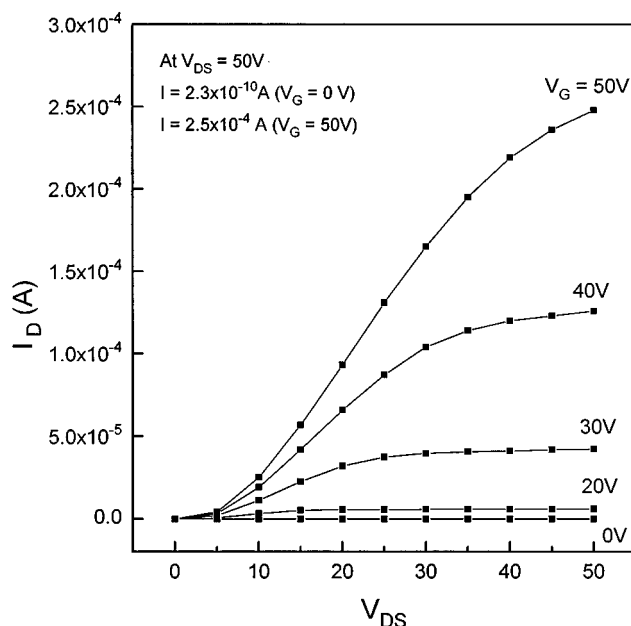


FIG. 1. Drain current (*I_D*) vs drain-source voltage (*V_{DS}*) for various gate voltages (*V_G*), for a C₆₀ thin film transistor.

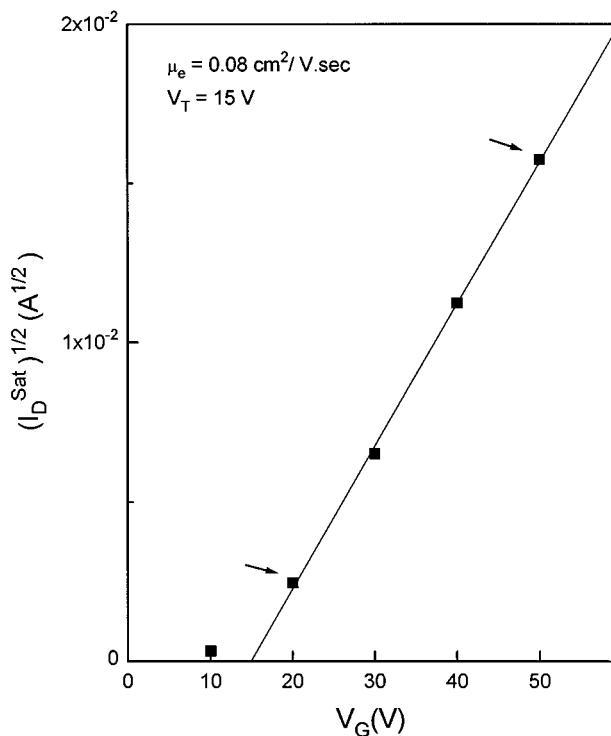


FIG. 2. Plot of the square root of the saturation current at the drain vs gate voltage (data from Fig. 1), together with the derived field effect electron mobility (μ_e) and threshold voltage (V_T).

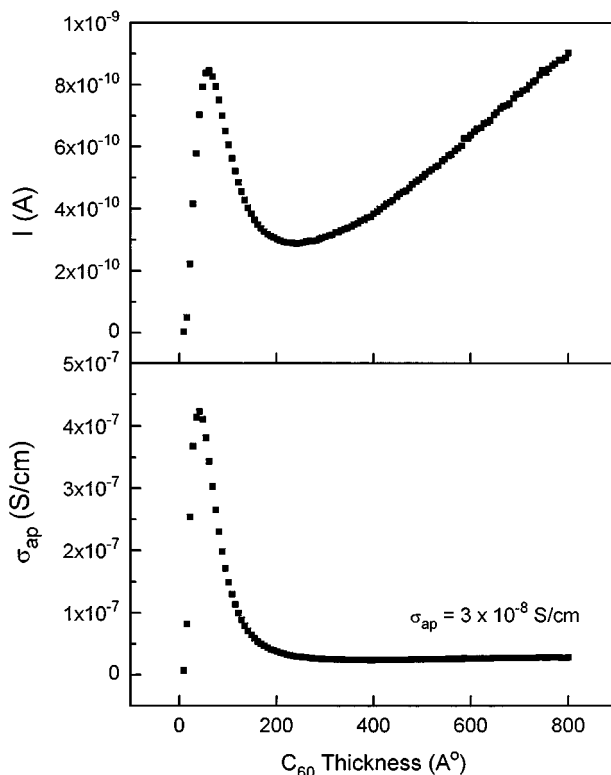


FIG. 3. (a) Drain-source current measured at 10 V, during the deposition of C_{60} on a thin film transistor. (b) Apparent conductivity (σ_{ap}), as a function of C_{60} film thickness (see text).

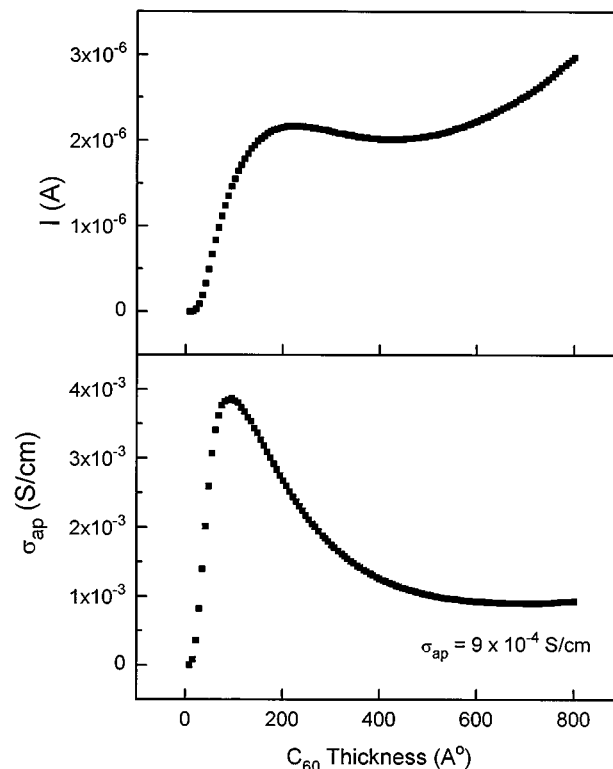


FIG. 4. (a) Drain-source current measured at 1 V, during the deposition of C_{60} on a thin film transistor that had been treated with TDAE. (b) Apparent conductivity (σ_{ap}), as a function of C_{60} film thickness (see text).

of the TFT given above. Even within these geometric approximations this quantity should be distinguished from a real conductivity because most of these devices do not exhibit ohmic behavior above about 1 V. The apparent conductivity rises very rapidly at the start of deposition due to carriers created at the C_{60} /substrate interface.

The nature of the substrate surface plays a critical role in the performance of the C_{60} devices. All of the films showed a peak in the apparent conductivity in the vicinity of a film thickness of 25–300 Å (Fig. 3), so there is charge transfer from the Au surface to the C_{60} film. In separate experiments using Cr contact pads we have established that Cr leads to higher conductivities and creates more carriers at the metal/ C_{60} interface than the Cr/Au multilayers used in this study. Thus the association of a conductivity with C_{60} films that are contacted with metal electrodes will be rather difficult. Even in the absence of intentional carrier injection, a C_{60} film on most metals behaves as an n -type doped semiconductor.

In testing the response of the TFTs to interface effects we found that the devices are extremely sensitive to the presence of amines on the substrate surface. Figures 4–6 show the results obtained with a substrate that had been treated with tetrakis(dimethylamino)ethylene (TDAE) entrained in flowing nitrogen, immediately before introduction into the UHV chamber. Even after overnight pumping and baking at 90 °C, the performance of the device is modified by the TDAE exposure. In the case of TDAE it is reasonable to expect that there is a thin layer charge transfer complex formed at the C_{60} /substrate interface as previous work has shown that TDAE is capable of reducing C_{60} .¹⁰

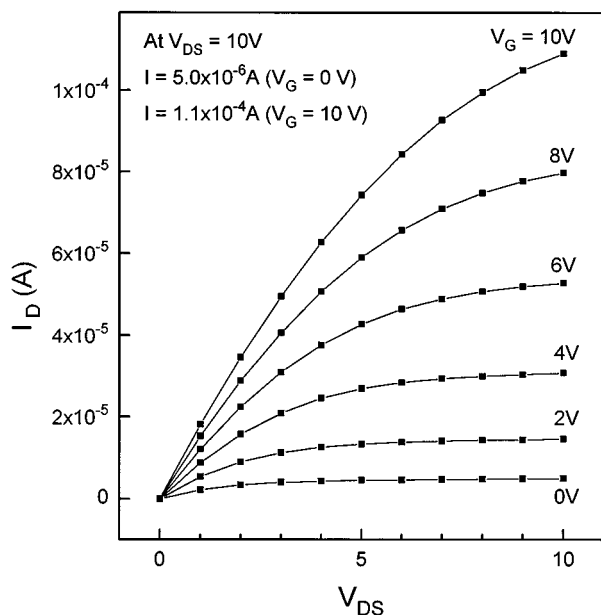


FIG. 5. Drain current (I_D) vs drain-source voltage (V_{DS}) for various gate voltages (V_G), for a C_{60} TFT on a substrate treated with TDAE.

Figures 5 and 6 show that the threshold voltage of the device is lowered to the point that it has become negative by the TDAE treatment. Furthermore the field effect mobility has increased by a factor of 3. *Ex situ* x-ray diffraction studies show no evidence for crystallinity in any of the films deposited in UHV, and irrespective of the surface treatment their diffraction patterns are characteristic of the granular

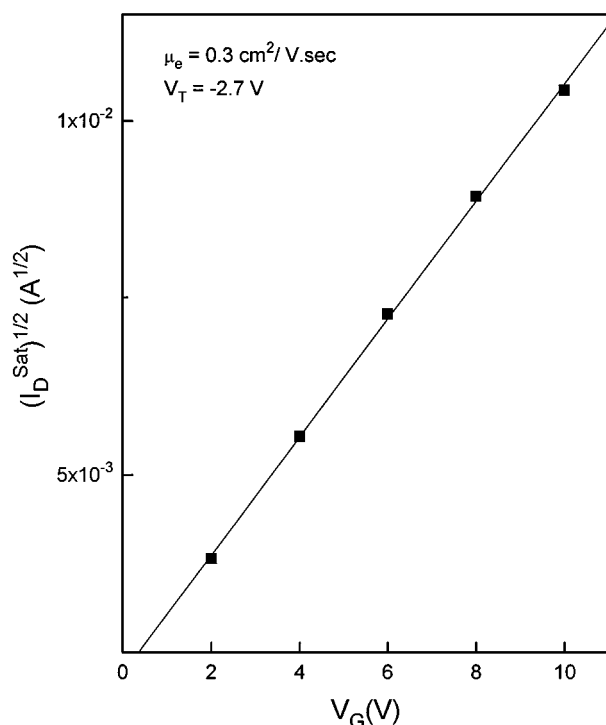


FIG. 6. Plot of the square root of the saturation current at the drain vs the gate voltage (data from Fig. 5), together with the derived field effect electron mobility (μ_e) and threshold voltage (V_T).

films normally found in this type of deposition experiment.⁷ The injection of electrons into organics from high work function metals is usually limited by the band offsets^{4,8} or in some cases by space charge effects.⁹ In the case of n -channel C_{60} both of these effects could be important in accounting for the low mobility and high threshold voltage in the devices not treated with TDAE, although four-point resistivity measurements on C_{60} films deposited on gold pads indicated negligible contact resistance. As the low mobility does not seem to originate from the film morphology it may be related to the interface states or space charge effects. In addition to these factors, the threshold voltage will also depend on the high barrier resulting from the band offsets between the gold work function and the C_{60} conduction band. The doping of the interface by TDAE would then be expected to both narrow the barrier width and increase the band bending, thereby lowering the threshold voltage and increasing the mobility of the injected carriers.

None of the thin film transistors operated in the atmosphere and exposure of the devices to the ambient lead to a rapid increase in the film resistivity by 4 or 5 orders of magnitude. Returning the devices to the UHV chamber, together with overnight baking restored the transistor behavior.

C_{60} films exhibit good device characteristics as the active element of thin film transistors. Because C_{60} forms isotropic solids, the films do not require particular attention to the control of molecular assembly that has proved crucial in other organic materials.¹ The field effect mobilities are among the highest seen in organic thin film transistors,^{1,2} although still below the value of $0.5 \pm 0.2 \text{ cm}^2/\text{V s}$ seen in time-of-flight measurements on C_{60} single crystals,¹¹ presumably because of interface effects. The high threshold voltages and sensitivity to oxygen probably both originate from the transport of charge by electrons rather than holes as is common in most organics. The difficulties of injecting electrons into organics from high work function metals is well known and the fact that the device performance is not degraded by exposure to nitrogen gas suggests that the oxygen molecules act as electron traps in the lattice of C_{60} molecules.

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